NASA TECHNICAL MEMORANDUM

NASA TM X-52852

NASA TM X-52852

THE DEGRADATION OF Cu_2S-CdS THIN FILM SOLAR CELLS UNDER SIMULATED ORBITAL CONDITIONS

by H. W. Brandhorst, Jr. and D. T. Bernatowicz
Lewis Research Center
Cleveland, Ohio

TECHNICAL PAPER proposed for presentation at
International Colloquium on Solar Cells sponsored by the
European Cooperation Space Environment Committee
Toulouse, France, July 6-10, 1970

THE DEGRADATION OF Cu_2S-CdS THIN FILM SOLAR CELLS UNDER SIMULATED ORBITAL CONDITIONS

by H. W. Brandhorst, Jr. and D. T. Bernatowicz

Lewis Research Center
Cleveland, Ohio

TECHNICAL PAPER proposed for presentation at

International Colloquium on Solar Cells sponsored by the
European Cooperation Space Environment Committee
Toulouse, France, July 6-10, 1970

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

E-5768

THE DEGRADATION OF Cu_2S-CdS THIN FILM SOLAR CELLS UNDER SIMULATED ORBITAL CONDITIONS

by H. W. Brandhorst, Jr.

and

D. T. Bernatowicz

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, U.S.A.

Abstract

Tests of Cu_2S-CdS thin-film solar cells under simulated low Earth orbit conditions have been made periodically over the past several years. The cells were found to degrade but the rate and amount of degradation varied considerably from cell to cell and test to test. An investigation was undertaken to determine the causes of the variability and the cause of the degradation itself.

Mechanical failure due to thermal stress was initially investigated but could not explain the results of the simulated space cycling tests. Rapid failure was subsequently observed when cells were illuminated while open-circuited. Progressive deterioration due to internal short circuiting was observed just as in some of the cycling tests. Filamentary conduction paths of copper coinciding with hotspots were found in the bulk of the cell. Various tests confirm the hypothesis that the filaments are the result of an electrochemical decomposition of Cu_2S with a threshold voltage between 0.35 and 0.40 V.

It is now believed that cells that degraded severely in early tests were operated near open-circuit voltage because of poorly selected load resistances. Results of current long-term tests in which the loads were carefully selected indicate a different, less severe mode of degradation also exists.

INTRODUCTION

Endurance tests of the Cu_2S-CdS solar cell have been made periodically for the past several years under simulated Earth orbital conditions. Essentially all cells that have been tested were manufactured by Clevite Corporation. They are nominally 7.5 cm x 7.5 cm in size with a Kapton plastic substrate and cover. Total cell thickness is about .01 cm.

Typically these tests have been conducted in liquid-nitrogen cooled vacuum chambers with a xenon arc solar simulator shining in through a window. The illumination was cycled by a shutter to give a one-hour illuminated period followed by a half-hour dark period. The cells were loaded by loosely selected resistors. Periodically the resistor was replaced by a variable load for tracing current-voltage (I-V) curves to monitor performance.

The cells degraded in all these tests. But there was a wide variation in degradation from cell to cell and from test to test. Results of an early test on cells made in October, 1967 are shown in figure 1 to illustrate the variation observed. The maximum power relative to the original maximum power is presented versus the number of sun/dark cycles. The worst cell degraded very quickly to less than half its original power in 320 cycles; the best cell degraded only 10%. The cells showed a substantial recovery during an interruption in the test, followed by a rapid redegradation when the test was resumed. Other tests made over the years have shown other widely varying results without any evident systematic trends. Generally, the short-circuit current, open-circuit voltage, and fill factor (maximum power/short-circuit current times open-circuit voltage) all fell as the cells degraded.

Obviously there was an unknown variable affecting the tests. A comprehensive effort was undertaken to identify and/or eliminate this unknown variable. Two approaches were taken. One was to reduce the variability among cells (by improved quality control and more stringent performance specifications) and to standardize and check testing and measurement procedures. The second approach was to search for the degradation mechanism by testing under unusually severe conditions and using new diagnostic techniques. This paper reports the results of this second approach, the search for the degradation mechanism.

RESULTS

Thermal Shock Tests

Mechanical failure due to thermal stresses was a suspected cause for the degradation. The large difference in thermal expansion coefficient between the cadmium sulfide and the Kapton cover and substrate induces thermal stresses in the solar cell package as the temperature is cycled. To test this hypothesis, thermal shock cycling tests were performed to exaggerate this mode of failure (ref. 1). In these tests, cells were repeatedly heated radiantly to 65°C for 5 minutes and then dipped into liquid nitrogen (-195°C) for 5 minutes. Figure 2 shows a typical cell after 250 cycles. The cell delaminated by splitting through the CdS layer. The lighter portion of the separated region was delaminated manually following the test. Measurement of cell output after the test showed a decrease in cell power and short-circuit current that was directly proportional to the delaminated area. However, the open-circuit voltage and fill factor did not change. This degradation mode was not typical of that observed in the space simulation tests. Therefore, it was concluded that thermal stresses were not the major cause of degradation and another mechanism was sought.

This is not to say that thermal stresses can be completely ignored. Delamination along the edges of a few percent of the total area has been observed on some cells in the space cycling tests.

Effect of Operating Voltage

Review of anomalous and supposedly spurious results that had been accumulated in the laboratory over the years suggested that the loading voltage was an important parameter. A simple test was run that incontrovertably showed that load voltage had a first order effect on degradation (ref. 2). In this test a cell in air at 25° was steadily illuminated (100 mw/cm^2) while the load across the cell was varied in steps. Output was measured by periodically tracing I-V curves. Figure 3 shows the maximum power (relative to its initial value) during the course of the test. Initially the cell was held at open-circuit voltage, and after 73 hours, the maximum power had dropped to 66% of its initial value. When the operating point was changed to the maximum power point, recovery was observed. After 27 hours the output had climbed to 86% of the initial value. The cell was then short-circuited, and further recovery to 95% was noted. Even during the storage in the dark some recovery was seen. At 608 hours the output was 97% of the original.

Degradation during Illumination at Open-Circuit

The I-V characteristics of a typical 7.5 cm x 7.5 cm CdS cell as it lost output under constant illumination at open-circuit is shown in figure 4 (ref. 3). The loss in open-circuit voltage and the change in slope near short-circuit is characteristic of a decreasing shunt resistance. This mode of degradation is similar to that of cells that degraded severely in the simulated orbital tests. The dark I-V characteristics also deteriorated under the illuminated open-circuit test. The dark characteristic changed from a rectifying to an ohmic characteristic as the cell degraded.

Degradation under Forward Bias without Illumination

The dark I-V characteristics of CdS solar cells were found to change when a forward current of 0.5 to 1.0 ampere was applied to unilluminated cells (ref. 3). In less than a minute, the I-V characteristic began a gradual transition toward an ohmic state. The failure of the unilluminated cell under forward bias is essentially identical to the failure under constant illumination condition, thus implying that only the sign and magnitude of the voltage are important.

Hotspots

Periodically during these tests, the temperature pattern on the cell surface was observed by means of an infrared imaging apparatus. Figure 5 shows a typical image displayed on an oscilloscope taken while current was passed through a degraded cell under forward bias in the dark. Regions of higher temperature have lighter shades of gray. Several localized hotspots can be seen on the cell. The temperature of the hotspot depended on the amount of current being passed through the cell. Temperatures in excess of 150°C were detected with a forward current of one ampere.

Better localization of the hotspots was possible by means of liquid crystals. The cell surface was painted with a liquid crystal solution that changed color between 30 and 32°C. Figure 6 shows a portion of a cell with hotspots made evident by liquid crystals; the hotspots are the distinct dark spots near the horizontal edge of the grid. As the current was reduced the hotspots got smaller and could be localized to a single grid wire. Nearly all hotspots coincided with a grid wire.

Correlation of Hotspots, Degradation, and Recovery

The appearance of hotspots correlated with the degradation of the illuminated and dark I-V curves of the cell. Furthermore, a way was found to make the hotspots disappear. When this was done, the I-V characteristics recovered. The most rapid recoveries were observed when a cell was reverse biased in the dark. Except with very severely degraded cells, a few minutes or less of reverse bias of about 1/2 volt would result in an abrupt change in the dark characteristic from the ohmic to the initial rectifying shape. At this time, no trace of the hotspot could be found. Also, the illuminated performance was improved, but not always to its initial level. Reexposure of the cell to illumination at open-circuit voltage would rapidly induce the original hotspot or another one to form. Also, the dark and illuminated characteristics could be restored by cutting the hotspot area out of the cell.

With severely degraded cells some recovery was seen after momentary interruptions of the illumination or reductions of the operating voltage. At times recovery was evident even while I-V curves were traced from open-circuit to short-circuit.

This evidence clearly pointed to a failure mechanism in which localized short-circuit paths develop in the cell. The formation of these shorting paths was related to the voltage across the cell and was at least somewhat reversible. However, there were no further clues as to the nature of these paths and the mechanism by which they formed.

Copper Nodules

The next clue came from investigators at the Clevite Corporation. While they were reproducing the degradation effects described above, they noticed the appearance of copper nodules on the surface of the cell (ref. 4). Figure 7 (ref. 5) shows a cross-section of one nodule of many found on a cell severely degraded under illuminated, open-circuit conditions. This nodule is about 0.05 mm high and 0.04 mm in diameter. The adjacent grid wire is 0.025 mm wide. Electron microprobe and chemical analyses confirm that the nodule is essentially pure copper.

Two sources of copper exist in these cells, the copper sulfide and the gold-plated copper grid wires. Cells with solid gold grids were tested, and they also developed hotspots and copper nodules. Therefore, the copper comes from the copper sulfide.

Surprisingly, the nodules did not coincide with hotspots, except when the nodules touched grid wires. However, formation of metallic copper indicated that basic changes were taking place in the cell and probably were related to the degradation.

Copper Filaments

Closer examination of a hotspot region was made by photomicrography (ref. 5). In this work a cell with a hotspot under a grid was cross-sectioned and painstakingly polished 5 to 6 μm at a time until the result shown in figure 8 was obtained. (The large lateral crack was caused by the polishing.) Fine filaments of copper can be seen running from the gold epoxy cement to the substrate. The bundle of filaments is about 5 µm in diameter. These filaments are believed to be the shorting path causing the hotspots and the degradation in output.

Threshold Voltage

Presumably the following decomposition occurs during nodule and filament formation:

$$Cu_2S \longrightarrow CuS + Cu$$

If a Cu_2S thickness of 1000 A° is assumed, there is sufficient copper within each grid opening (0.4 x 2.5 mm) for the formation of two nodules of the size shown in figure 7.

The electrode potential for this reaction at 25°C was calculated from published values of the free energies (ref. 6). The calculated value is - 0.386 volt.

Some simple experiments were made to check whether there was indeed such a threshold voltage for the growth of copper in these cells. A pointed gold electrode was rested on the copper sulfide surface of a cell without a grid. The electrode was made negative with respect to the back cell electrode. When the applied voltage was between 0.38 and 0.40 volts, copper grew out from under the gold point in a fern-like fashion along the surface of the copper sulfide. When the voltage was reduced to between 0.35 and 0.36 volts, no copper grew even though more than twice as many coulombs of charge were passed between the electrodes.

Simulated Space Cycling Tests at Constant Load

To determine if there was a threshold voltage for degradation in simulated space cycling, a special test was run (ref. 7). In this test, the voltage across the cell was controlled by a load resistor that was not varied or disconnected throughout the test. Resistors were sized to give a range of initial operating voltage from low to near open-circuit. The earlier practice of tracing I-V curves to monitor performance during the test was not used. The maximum power was determined from I-V curves taken before and after the test. Figure 9 shows the results after 1429 cycles. The final power for each cell, relative to its initial value, is shown versus its operating voltage at the start of the test. As expected, the degradation is greater for the cells at the highest voltages. At the lower voltages the degradation is independent of voltage. There does appear to be a threshold between 0.35 and 0.40 volts. Fortuitously this threshold appears to be sufficiently higher than the maximum power voltage of 0.30 that it can be avoided in most applications.

Similar testing procedures have now been adopted for all long-term space simulation tests of Cu_2S-CdS thin-film solar cells. During the test, cell performance is computed from the voltage drop across the fixed load resistance sized for maximum power. The resistance is not changed throughout the test. The longest test to date, and still in progress, is being conducted in this way at The Boeing Company under NASA contract. Four cells have been exposed to more than 5000 cycles of 1 hour sun/$\frac{1}{2}$ hour dark. Figure 10 shows the relative power of the best and the worst cells (i.e. those with the least and the most degradation). After 5000 cycles the best had degraded only 7% and the worst 20%; the average degradation for the four cells was 12%.

The early test results from figure 1 are also shown for comparison. There is a marked difference in the rates of degradation. It is now believed that the cells that had degraded severely in early tests were operated near open-circuit voltage because of poorly chosen load resistors. The relatively slow degradation seen in the later test is believed to be due to a different, but yet unknown, mechanism.

Review of Modes of Degradation

Since the cause of the relatively slow degradation still seen in the cycling tests is unknown, it may be of value to contrast the three modes characteristic of (1) thermal shock cycling, (2) constant illumination at open-circuit voltage, and (3) periodic illumination in vacuum with constant maximum-power load resistance (simulated space cycling at constant load). These observations have come from I-V curves made before and after the tests. However, in situ measurements, where available, confirm these trends. With thermal shock cycling, short-circuit current is lost while open-circuit voltage and fill factor remain constant. The loss in current is proportional to the loss in area. Under illumination at open-circuit voltage, both the fill factor and the open-circuit voltage drop while the short-circuit current remains the same. This indicates a shorting of the cell which is confirmed by the presence of hotspots. Finally, under the simulated space cycling tests, there is a loss of short-circuit current, a larger loss in fill factor but a slight increase in the open-circuit voltage. The reasons behind the loss in current and fill factor and gain in open-circuit voltage are not clear. Some of the loss in current may be due to cracking or delamination caused by thermal stresses. Also, the changes bear a similarity to those caused by heat treatment of Cu_2S-CdS cells (ref. 8). In that case, short-circuit current decreases and the open-circuit voltage increases also. However, in this case the fill factor generally increases. Whether this similarity extends to the physical processes taking place is open to speculation.

CONCLUSION

The cause of the severe degradation of Cu_2S-CdS thin-film solar cells has been found. When the operating voltage is sufficiently high, an electrochemical decomposition of Cu_2S produces metallic copper. Some of this copper grows as filaments through the cell, forming short-circuits that reduce the output of the cell. The short-circuit locations can be readily observed as hotspots.

The electrochemical reaction has a threshold voltage between 0.35 and 0.40 V. (Cu_2S positive). When the cell is operated at voltages exceeding this threshold, for example at open-circuit voltage (about 0.47 V), rapid degradation occurs.

Fortuitously, the threshold voltage is higher than the voltage for maximum power, about 0.30 V. There appears to be sufficient margin here that the cells could be used in power-producing applications without exceeding the threshold for this degradation mechanism.

It is now believed that cells that degraded severely in early tests were operated near open-circuit voltage because little attention was given to the selection of load resistances. In current long-term space cycling tests for which the load resistances have been carefully matched to the cells this severe degradation has not been seen. However, there remains a different, less severe mode of degradation due to an unknown cause. In the longest test to date the average degradation of four cells was only 12% after 5000 cycles or 7500 hours.

REFERENCES

1. Smithrick, John J.: Effect of Thermal-Shock Cycling on Thin-Film Cadmium Sulfide Solar Cells. NASA TM X-1819, 1969.

2. Spakowski, A. E.; and Forestieri, A. F.: Observations on CdS Solar Cell Stability. Presented at the IEEE Photovoltaic Specialists Conference, Pasadena, California, Nov. 19-21, 1968.

3. Scudder, Larry R.; Godlewski, Michael P.; and Klucher, Thomas M.: Observations of Degraded CdS Solar Cells. NASA TM X-52668, 1969.

4. Shirland, F. A.; Bower, W. K.; Dunn, W. F.; and Green, J. B.: CdS Solar Cell Development, Clevite Corp. (NASA CR-72534), Mar 1969.

5. Godlewski, Michael P.; Bozek, John M.; and Scudder, Larry R.: Observations of Hotspots and Metallic Deposits in CdS Thin-Film Solar Cells. NASA TM X-52697, 1969.

6. Latimer, Wendall M.: Oxidation Potentials. Second ed., Prentice-Hall, Inc., 1952.

7. Smithrick, John J.: Proposed NASA Technical Memorandum.

8. Gill, William D.: Mechanism of the Photovoltaic Effect in II-VI Compounds. Ph. D. Thesis, Stanford University, 1969.

E-5768

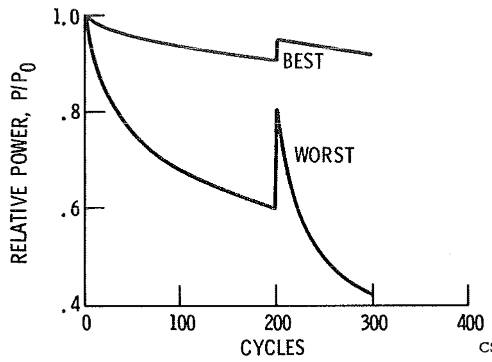
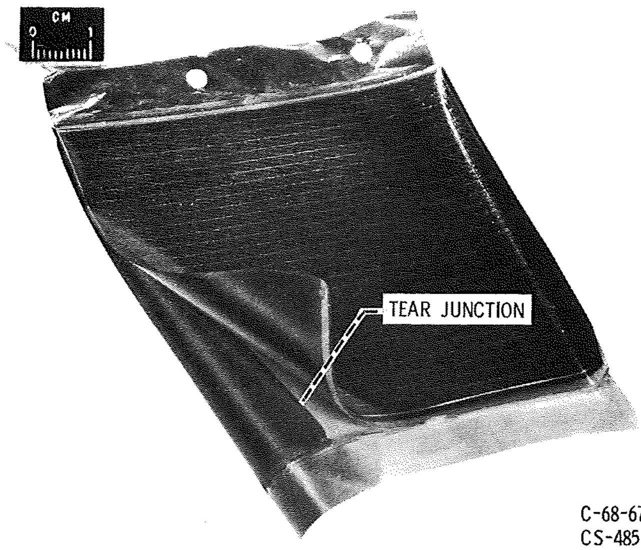


Figure 1. - Change in power output of Cu_2S-CdS thin-film solar cells during a space cycling test. Sun/dark cycle was 60 min/30 min. The cells were made in October 1967.



C-68-670
CS-48577

Figure 2. - A Cu_2S-CdS thin film solar cell delaminated by 250 thermal shock cycles. Substrate and cover are Kapton.

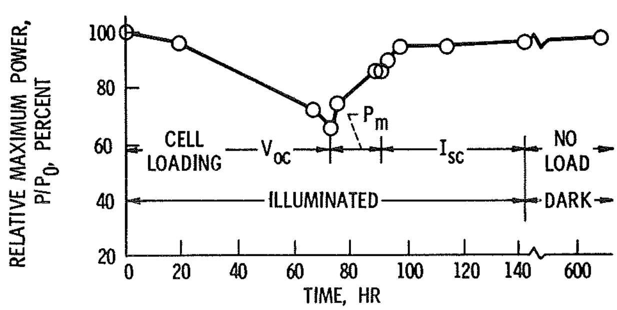


Figure 3. - Change in maximum power output of a Cu_2S-CdS solar cell after various loading conditions.

E-5768

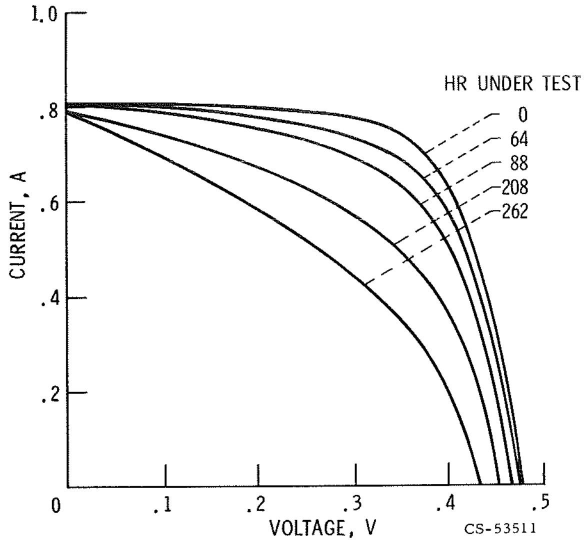
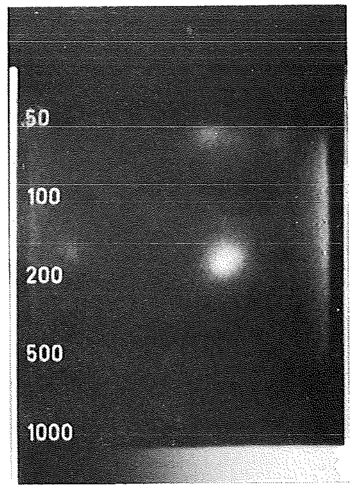


Figure 4. - Change in current-voltage characteristic of a 7.5x7.5 cm Cu_2S-CdS solar cell after illumination at open-circuit.



CS-53513

Figure 5. - Infrared image of a degraded 7.5x7.5 cm cell showing hotspots.

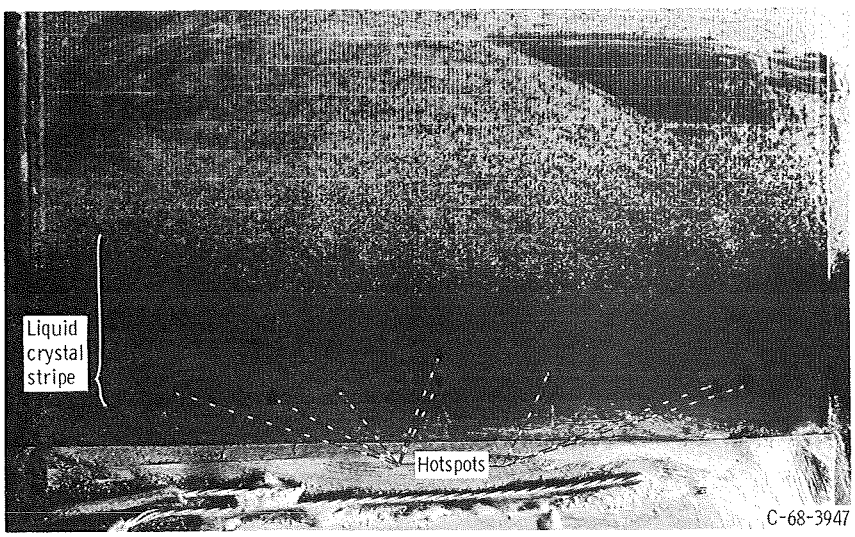


Figure 6. - Imaging of hotspots with a liquid crystal solution changing color between 30 and 32° C.

E-5768

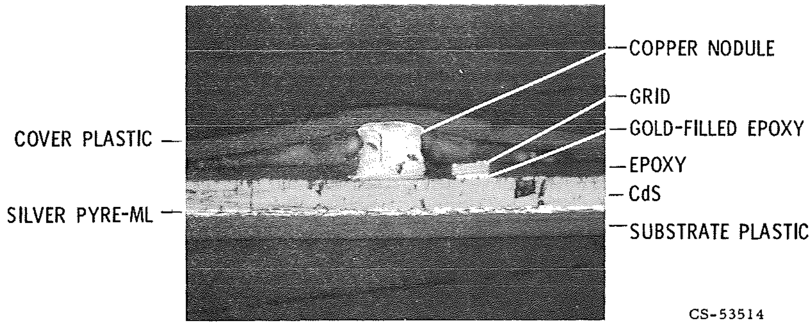


Figure 7. - Cross-section photomicrograph of a copper nodule on a severly degraded cell.

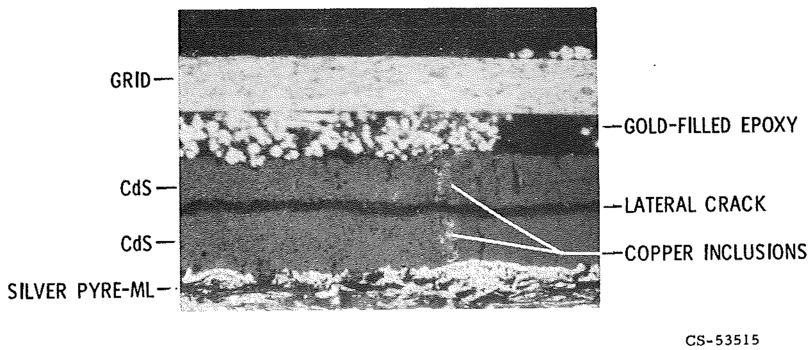


Figure 8. - Cross-section photomicrograph of copper inclusions or filaments in a hotspot region.

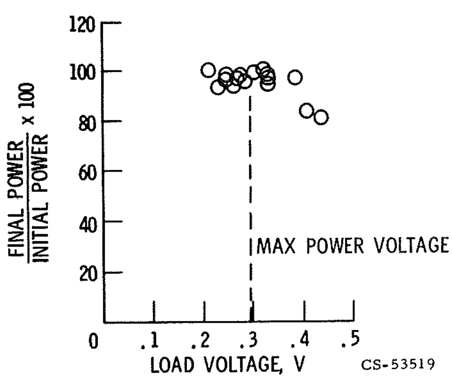


Figure 9. - Effect of load voltage on maximum power output of Cu_2S-CdS solar cells after simulated space cycling through 1429 cycles of 60 min Sun/30 min dark. Load resistance was not changed during test.

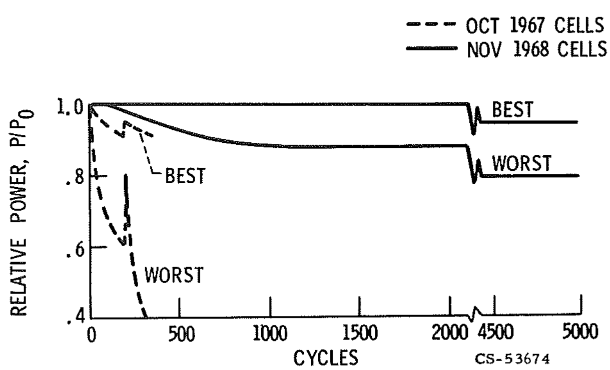


Figure 10. - Change in power output of Cu_2S-CdS solar cells during space cycling tests. Sun/dark cycle was 60 min/30 min. Cells made in November 1968 were tested with constant resistance load sized for maximum power. The 1967 cells had unknown loads.